



PATENT COOPERATION TREAT

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PHN 17.710W0	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/EP 00/ 11005	International filing date (day/month/year) 06/11/2000	(Earliest) Priority Date (day/month/year) 11/11/1999
Applicant KONINKLIJKE PHILIPS ELECTRONICS N.V.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 03 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

4

☐ None of the figures.

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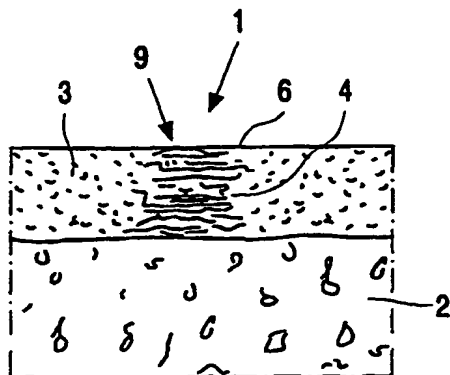
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: **OUTER LAYER AND ELEMENT WITH MARKINGS, AND METHOD OF MANUFACTURING SAME**



(57) Abstract: A marking (4, 5) is formed in an outer layer (3; 23; 43) comprising a polymer material with an inorganic main chain and with certain visual properties by at least one region (9; 29; 49) of the outer layer (3; 23; 43) of which at least one of the visual properties shows a deviation, visible to the human eye, from the same property in other regions (9; 29; 49?) of the outer layer (3; 23; 43). Since the marking (4, 5) is obtained by means of at least a locally changed visual property of material of the outer layer (3; 23; 43) itself, the marking (4, 5) does not constitute a substantial interruption of the outer layer (3; 23; 43), and the application of the marking (4, 5) does not cause any substantial unevennesses in the outer layer (3; 23; 43). The following are further described: an element having such an outer layer (3; 23; 43) and a method of applying such a marking (4, 5).

WO 01/34401 A1

Outer layer and element with markings, and method of manufacturing same

The invention relates to an outer layer comprising a polymer material with certain visual properties and to an element having such an outer layer.

5 An example of an element having such an outer layer and designed for consumer products is known from US patent 5,592,766. This element is constructed as a sole plate of an electric iron. The outer layer is particularly suitable for such an application because it has very good sliding properties during ironing, a high resistance to scratching, can be easily cleaned, can be provided in a simple manner and at low cost against the soleplate, is well
10 resistant to corrosion, and is resistant to fast temperature changes up to 300 °C. Examples of alternative applications in elements for consumer products, where a layer of polymer material with an inorganic main chain is particularly suitable on account of at least a number of the above properties, are surfaces which come into intensive sliding contact with the user's skin, such as portions of electric-shaver heads, barbers' implements, writing tools and other tools or
15 mechanically loaded surfaces which are fairly strongly heated during use and which should be easy to clean, such as hot plates and oven walls.

 It is a problem to provide such outer layers with markings without the latter causing interruptions in the outer layer, where the protective effect of the outer layer would be absent, or spots of roughness in the outer layer, where dirt can accumulate and which
20 adversely affect the sliding properties.

 It is an object of the invention to provide a solution to the above problem.

 This object is achieved according to the invention in that the outer layer is
25 provided with a marking formed by at least a region of said outer layer of which at least one of said visual properties is different from the corresponding property of other regions of said outer layer, which difference is visible to the human eye.

 The invention further relates to an element provided with such an outer layer, and to a method of marking an outer layer comprising a polymer material with an inorganic

main chain and having visual properties, which method comprises the provision of changes visible to the human eye in at least one of said visual properties in at least one region of said outer layer, whereby said at least one region forms a visible marking in said outer layer when viewed frontally.

5 Since the marking is obtained by means of at least one locally changed visual property of the material of the outer layer itself, the marking does not constitute a substantial interruption in the outer layer, and the provision of the marking does not cause any substantial unevennesses in the outer layer.

10 Particular embodiments of the invention have been defined in the dependent claims.

Further objects, aspects, effects, advantages, and details of the invention will become apparent in the following description of a few embodiments of the invention, for
15 which reference is made to the drawing, in which

Fig. 1 is a bottom view of a sole of an electric iron,

Fig. 2 is a cross-sectional view on an enlarged scale of a portion of the sole of the electric iron of Fig. 1 which has not been treated for providing a marking,

20 Fig. 3 is a cross-sectional view on an enlarged scale of a portion of the sole of the electric iron of Fig. 1 which has been treated for the provision of a marking,

Fig. 4 is a diagrammatic picture of a marking as partly shown in Fig. 3,

Fig. 5 is a diagrammatic cross-sectional view of a boundary area of a carrier and a layer of polymer material in an alternative embodiment, and

25 Fig. 6 is a diagrammatic cross-sectional view of a boundary area of a carrier and a layer of polymer material in a further alternative embodiment.

An example of an element according to the invention is formed by the sole 1 of an electric iron shown in various ways in Figs. 1 to 4.

30 This sole is built up inter alia from a carrier 2 of metal or a metal alloy which supports an outer layer 3. This outer layer 3 forms a sliding or contact layer 3 of the sole 1. Said outer layer 3 is formed from a polymer material, in this example on the basis of polysilicate which was provided in a sol-gel process. The main chain or backbone of the polymer is inorganic; any lateral chains or branches may be organic, if so desired. The outer

layer 3 is provided with markings in the form of decorative lines 4 and characters 5. The latter may form, for example, a type indication.

The outer layer 3 in which the markings 4, 5 are provided was obtained in that a sol-gel substance was provided on the carrier 2, and the sol-gel substance was subsequently converted into the polymer material with an inorganic main chain of the outer layer 3.

The markings 4, 5 are formed in that visual properties – in this example shade of darkness and color – of regions 9 of the outer layer 3 exhibit a clearly visible difference from the corresponding visual properties of the other regions of the outer layer 3. In this example, the outer layer has a yellow ochre color, whereas the markings are of a darker color and more brownish. Since the markings form part of the outer layer 3, their presence has no substantial negative effect on the sliding properties of the outer layer, the protective effect of the outer layer 3, and the dust-repellent properties of the outer layer 3.

When the markings 4, 5 are provided, changes are applied in the visual properties of the outer layer 3 in those regions of the outer layer 3 which are destined to form the markings 4, 5 in the outer layer when viewed frontally.

Compared with the separate provision of portions of the outer layer 3 with deviating visual properties in the areas of the markings, the above offers the advantage that the provision of the outer layer 3 can be carried out in one step or series of steps. It is further achieved thereby that the markings 4, 5 are formed integrally with other portions of the outer layer 3, so that the screening effect of the outer layer 3 over the surface of the sole 1 remains intact also after a long period of use and a corresponding large number of fast and major temperature changes. As is evident from Fig. 3, the outer layer 3 may be locally very thin, or locally interrupted after treatment. Such a minor local defect in the outer layer 3 does not adversely affect the durability of the outer layer 3.

The changes in the visual properties discussed above are obtained in a very efficient manner through the local supply and absorption of energy in those regions which are to form the markings 4, 5. The supply of energy to the outer layer seems to have the effect that bonds between the polymer chains and lateral branches are broken. Ionization of the chains may also play a part. The result is that at least one visual property of the outer layer changes.

If the element, such as the sliding layer in this example, is designed to transfer heat during operation, and especially if also the energy is supplied in the form of heat, it is important that the results of the local energy supply as regards the speed of the temperature change or the level of the temperature achieved surpass the speed of change or the temperature which occur during normal use.

It is furthermore advantageous for an effective marking if the inorganic main chain of the material of the outer layer has organic lateral branches. These may be made to discolor comparatively easily, while the inorganic main chain is not or hardly affected, so that the mechanical properties of the outer layer are substantially maintained.

5 If the outer layer is designed to be heated during operation, it is advantageous when the organic lateral branches comprise methyl groups. These may be easily made to discolor by heating on the one hand, while on the other hand they are heat-resistant to such a degree that substantially no discoloration will occur at temperatures prevailing in household applications such as ironing and keeping coffee hot.

10 The energy transfer may take place, for example, through contact with a heat source or in the form of radiation.

A particularly accurate and efficient treatment may here be achieved if, as in the present example, the energy supply is realized in that the sole 1 is operated upon with a laser beam. A large number of different markings, including very fine patterns, can be provided in
15 that the laser beam is controlled in a suitable manner and/or in that suitable masks are used.

The laser treatment is carried out such that a substantial portion of the laser beam is absorbed by the outer layer 3. The energy released during the absorption of the laser radiation by the outer layer 3 causes changes in the visual properties of the outer layer 3. An advantage of this is that the outer surface 6 of the outer layer 3 remains entirely or
20 substantially in its original condition, and accordingly retains substantially the same properties as the portions of the outer layer 3 situated outside the regions of the markings 4, 5. The outer surface 6 of the outer layer 3 remains sufficiently flat and substantially continuous after the treatment, so that the treated regions will have substantially the same mechanical properties as the non-treated regions.

25 Favorable results are obtained when a laser beam is used with a wavelength of 800-1600 nm, in particular 1000-1100 nm. It is furthermore advantageous for an efficient utilization of the laser energy when the laser has a wavelength at which the outer layer has a comparatively strong absorption.

To obtain a sharp delineation of the markings 4, 5, it is furthermore
30 advantageous that a sol-gel treatment renders it possible to form a very thin outer layer, for example with thicknesses below 50 μm , or even below 25 or 30 μm . In addition, the outer layer 3 is dull-translucent, which enhances the contrast between markings 4, 5 in the zone of the outer layer 3 adjoining the carrier 2 and surrounding regions of the outer layer 3.

The carrier 2 is manufactured from an aluminum alloy. This is advantageous for the fast removal of heat released during the absorption of the laser radiation, whereby firstly a strong thermal shock effect can be obtained in the outer layer 3, and secondly the effect of released heat remains limited to a small region of the outer layer 3.

To obtain a satisfactory application and adhesion, it is furthermore advantageous that the sol-gel substance from which the outer layer 3 is obtained comprises monomers for the formation of the polymer material and 3-glycidyloxypropyltrimethoxysilane (glymo), the quantity of the 3-glycidyloxypropyltrimethoxysilane being less than 50% by weight of the quantity of the monomers. This effect is particularly apparent if the sol-gel substance comprises an alkoxy silicate as the monomer for the formation of the polymer material.

The laser beam with which the regions for the formation of the markings 4 and 5 are treated is a pulsating laser beam in this embodiment. To obtain a distinct marking without excessive attacks on the outer layer 3, it is advantageous here to carry out the pulsatory irradiation with a pulse duration shorter than 30 ns, and in particular shorter than 20 ns.

There are many alternative possibilities for providing the markings 4, 5, and many alternative products which can be obtained thereby, in addition to the example described above of the manner of providing markings and the product obtained thereby in accordance with the embodiment described above.

Fig. 5 shows an example where the outer layer 23 of inorganic polymer material provided on a carrier 22 comprises fillers in the form of particles 24 which have a visual property in the form of their degree of darkness, which can be influenced by a laser. The particles 24 have a darker hue in a region 29 owing to the action of laser beams, thus forming a marking. The fillers prevent the laser radiation from penetrating deeply into the outer layer 23. As a result, substantially exclusively particles in an outermost zone of the outer layer 23 have been discolored in the region 29 of the marking. It is preferable with the use of colored fillers to choose a wavelength for the laser radiation which does not correspond to or is far removed from the wavelength of the color of the fillers so as to promote the effectivity of the laser irradiation.

The fillers preferably comprise fluorided hydrocarbons. This offers the advantage that the fillers at the same time enhance the gliding properties and the water-repelling action of the outer layer 23.

In another embodiment shown in Fig. 6, the outer layer 43 is built up from several (in this example two) layers 50, 51 of an inorganic polymer material. The outer layer 50 has been removed in the region 49 which forms the marking, so that the layer 51 adjoining the carrier 42 is visible. The two layers 50, 51 have clearly differing visual properties, so that a clear marking in the outer layer 43 is obtained in this manner. The removal of the outer layer 50 may again be carried out by means of a laser, but it may also be realized by alternative, for example mechanical means.

In the case of an outer layer composed of two layers having different visual properties, it is also possible to keep the outermost layer at least substantially intact and to change a subjacent layer visually through an action from the outside, for example in that it is made to melt or made to change its color or degree of darkness. This may be achieved, for example, in that the absorption of the radiation is caused to take place selectively in the layer adjoining the carrier and/or in the carrier, and/or in that the layers are so constructed that the layer adjoining the carrier reacts differently to the external action than does the outermost layer.

The outer layer may in principle be self-supporting or may be provided on a different type of carrier, for example made of glass or ceramic material. Furthermore, the outer layer may be a shaver head or a control panel, or it may serve as an easily cleanable protective layer, for example of a hot plate of a coffee maker, instead of as a sliding layer of, for example, an ironing sole.

In view of the above it will be clear to those skilled in the art that many alternative embodiments may exist and be created in addition to those described above.

CLAIMS:

1. An outer layer comprising a polymer material with an inorganic main chain and having certain visual properties, characterized by a marking (4, 5) formed by at least a region (9; 29; 49) of said outer layer (3; 23; 43) of which at least one of said visual properties is different from the corresponding property of other regions of said outer layer (3; 23; 43),
5 which difference is visible to the human eye.
2. An outer layer as claimed in claim 1, wherein said at least one region (9; 29; 49) forming said marking (4, 5) is substantially integral with other portions of said outer layer (3; 23; 43).
10
3. An outer layer as claimed in claim 1 or 2, wherein at least one of said visual properties of said at least one region (9; 29; 49) forming said marking (4, 5) is modified through the influence of laser radiation.
- 15 4. An outer layer as claimed in any one of the preceding claims, wherein the outer layer (3) is at least dull-translucent.
5. An outer layer as claimed in any one of the preceding claims, formed by a sol-gel process.
20
6. An outer layer as claimed in any one of the preceding claims, further comprising filler materials (24) with visual properties of which at least one can be changed by means of a laser.
- 25 7. An outer layer as claimed in claim 6, further comprising fluorided hydrocarbons.
8. An outer layer as claimed in any one of the preceding claims, comprising at least two layers (50, 51) of polymer material with an inorganic main chain, wherein said at

least two layers are absent, with the exception of at least one layer thereof, in the at least one region (49) which forms said marking.

9. An outer layer as claimed in any one of the preceding claims, wherein said
5 inorganic main chain has organic lateral branches.

10. An outer layer as claimed in claim 9, wherein said organic lateral branches
comprise methyl groups.

10 11. An element with a carrier structure (2; 22; 42) which support an outer layer (3;
23; 43) as claimed in any one of the preceding claims.

12. An element as claimed in claim 11, wherein the material of the carrier structure
(2; 22; 42) is a hard material of permanent shape, such as a metal or a metal alloy, a ceramic
15 material, a glass, or hard plastic.

13. An element as claimed in claim 12, further comprising an anodized layer which
supports said outer layer (3; 23; 43).

20 14. An element as claimed in any one of the claims 11 to 13, wherein said outer
layer (3) in said at least one region (9) is substantially unchanged in a zone adjoining an outer
surface of said outer layer (3) as compared with a zone of surrounding areas of said outer layer
(3) which adjoins an outer surface of said outer layer (3).

25 15. A method of marking an outer layer (3; 23; 43) comprising a polymer material
with an inorganic main chain and having visual properties, which method comprises the
provision of changes visible to the human eye in at least one of said visual properties in at
least one region (9; 29; 49) of said outer layer (3; 23; 43), whereby said at least one region (9;
29; 49) forms a visible marking (4, 5) in said outer layer (3; 23; 43) when viewed frontally.

30

16. A method as claimed in claim 15, wherein the outer layer (3; 23; 43) in which
said marking (4, 5) is provided was obtained through the application of a sol-gel substance
onto a carrier (2; 22; 42) and through the conversion of said sol-gel substance into said
polymer material with an inorganic main chain.

17. A method as claimed in claim 16, wherein the sol-gel substance comprises an alkoxy silicate as the monomer for the formation of said polymer material.

5 18. A method as claimed in any one of the claims 15 to 17, wherein said changes in at least one of said visual properties are obtained through a local energy supply to said at least one region (9; 29; 49) which forms said marking (4, 5).

10 19. A method as claimed in claim 18, wherein said local energy supply is provided by a laser beam.

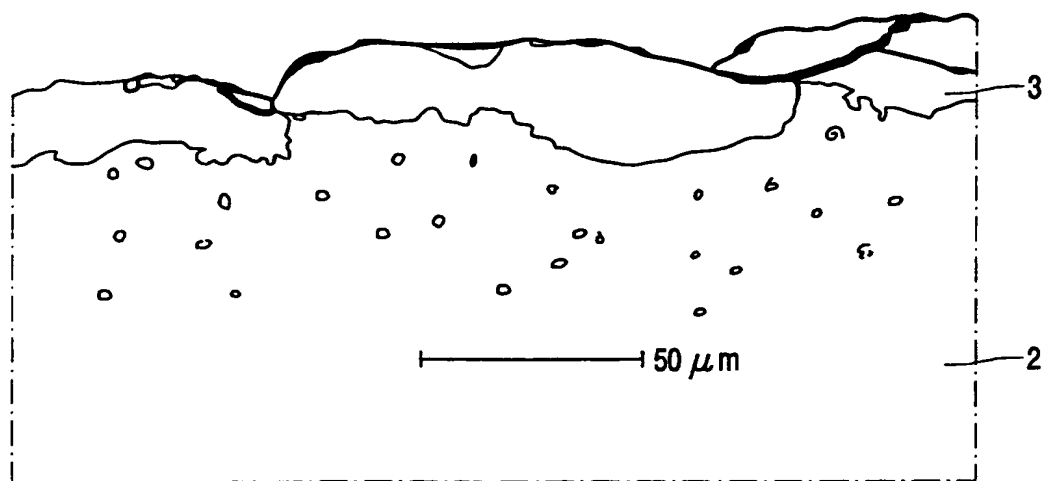
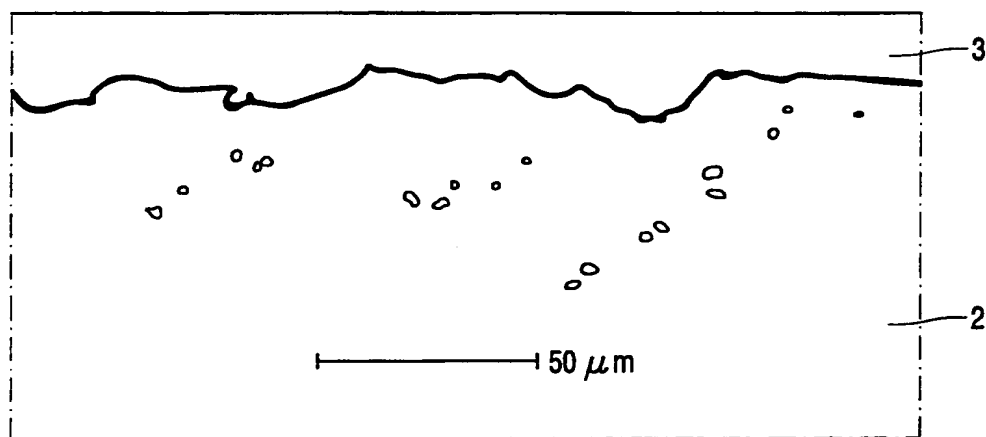
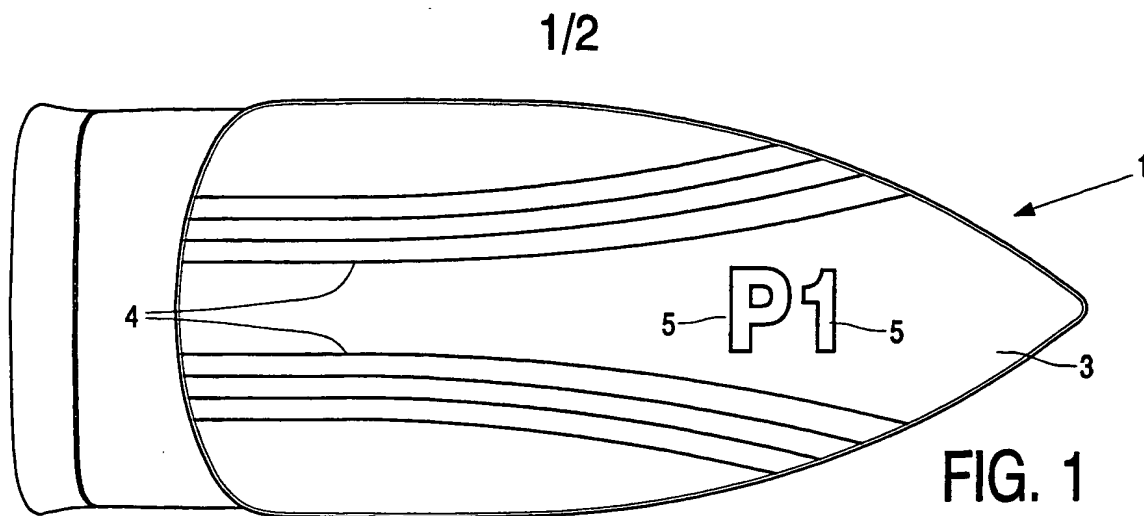
20. A method as claimed in claim 19, wherein a substantial portion of said laser beam penetrates said outer layer (3) and is absorbed by a carrier which supports said outer layer (3).

15

21. A method as claimed in claim 19 or 20, wherein said laser beam is a pulsating laser beam, and wherein the pulsation is carried out with a pulse duration shorter than 30 ns, preferably shorter than 20 ns.

20 22. A method as claimed in claim 19 or 20, wherein said laser beam has a wavelength of between 800 and 1600 nm, preferably between 1000 and 1100 nm.

23. A method as claimed in any one of the claims 19 to 21, wherein the laser has a wavelength at which the outer layer shows a comparatively strong absorption.



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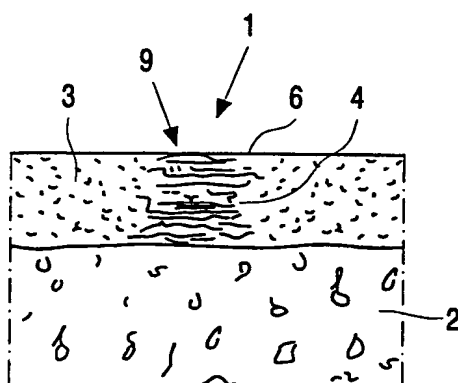


FIG. 4

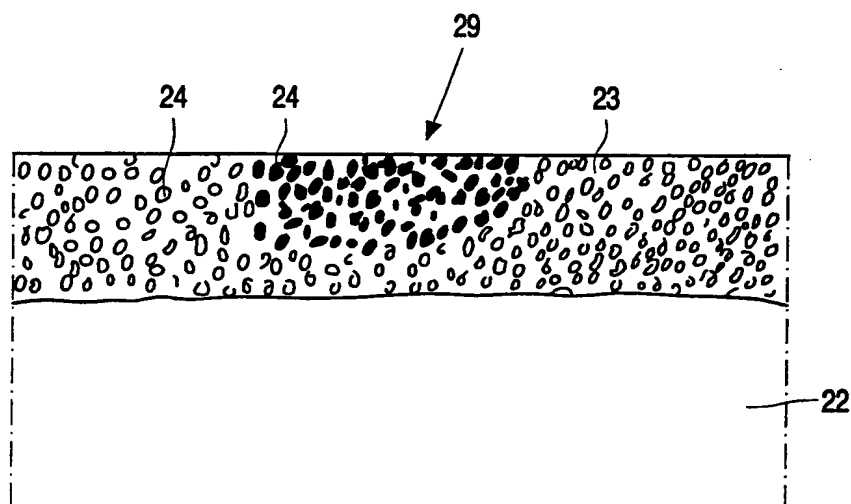


FIG. 5

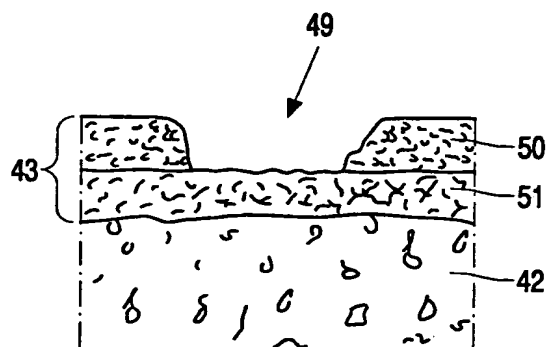


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B41M5/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 853 955 A (TOWFIQ FOAD) 29 December 1998 (1998-12-29) ✓	1-6, 9-12, 14-20
Y	column 1, line 65 -column 2, line 51 column 9, line 41 - line 55 ---	7
Y	US 5 789 466 A (BIRMINGHAM JR JOHN NICHOLAS ET AL) 4 August 1998 (1998-08-04) column 2, line 5 - line 45 --- -/--	7



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

2 March 2001

Date of mailing of the international search report

09/03/2001

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/11005

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 855 969 A (ROBERTSON JOHN A) 5 January 1999 (1999-01-05)	1-4, 9-12, 14, 15, 17-20, 23
Y	column 2, line 35 - line 55 column 3, line 1 - line 10 column 4, line 5 - line 20 column 5, line 7 - column 6, line 5 -----	13
X	DE 44 46 874 A (FOBA FORMENBAU GMBH ; BAYER AG (DE)) 4 July 1996 (1996-07-04) page 2, line 18 - page 3, line 11; claims 1-3 -----	1-6, 8, 15, 18, 19, 21-23
X	EP 0 710 570 A (QUANTUM CHEM CORP) 8 May 1996 (1996-05-08) page 4, line 9 - line 28 page 5, line 43 - page 6, line 23 page 7, line 6 - line 25 -----	1-4, 6, 8-11, 13-15, 17-23
Y	FR 2 649 628 A (DUVICQ ETS CHARLES) 18 January 1991 (1991-01-18) page 1, line 4 - page 2, line 16 -----	13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/11005

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5853955	A	29-12-1998	NONE	
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